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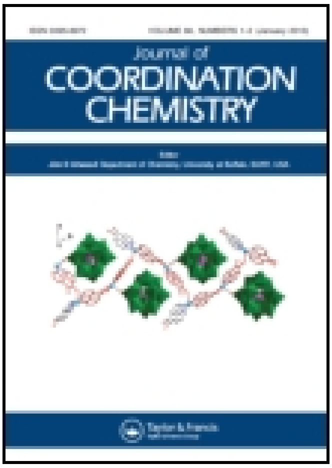

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Syntheses, structures and photochromic properties of two tetrazolylazo-based K^+ and Cd^{2+} complexes

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Syntheses, structures and photochromic properties of two tetrazolylazo-based K^+ and Cd^{2+} complexes

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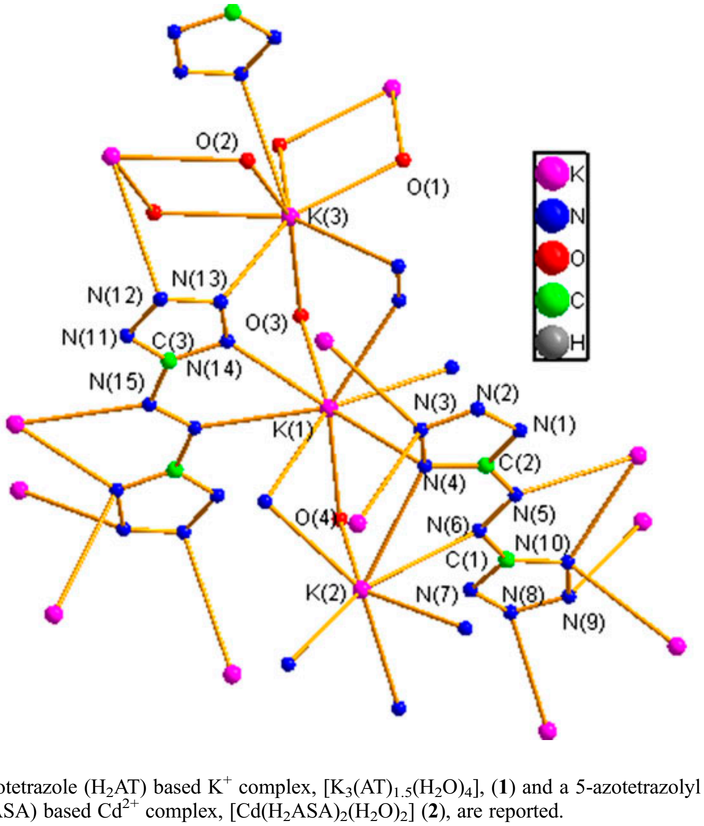

A 5,5′-azotetrazole (H_2AT) based K^+ complex, $[K_3(AT)_{1.5}(H_2O)_4]$, (**1**) and a 5-azotetrazolyl salicylic acid (H_3ASA) based Cd^{2+} complex, $[Cd(H_2ASA)_2(H_2O)_2]$ (**2**), are reported.

A 5,5′-azotetrazole (H_2AT)-based K^+ complex of $[K_3(AT)_{1.5}(H_2O)_4]$ (**1**) and another 5-azotetrazolyl salicylic acid (H_3ASA)-based Cd^{2+} complex $[Cd(H_2ASA)_2(H_2O)_2]$ (**2**) have been synthesized and characterized by single-crystal X-ray diffraction analysis. Complex **1** shows a 3-D structure formed

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by two μ_7- and μ_8-bridging trans-AT^{2-} ligands and μ_2-bridging waters linking three kinds of K^+ ions. Complex **2** features a 1-D chain structure in which each trans-enol H_2ASA^- anion is a μ_2-bridging ligand with one N(tetrazole) atom and one O(carboxyl) coordinating to two different Cd^{2+} ions. The photochromic and photoluminescent properties for aqueous solutions of **1** and **2** were investigated.

Keywords: 5,5′-Azotetrazole; 5-Azotetrazolyl salicylic acid; Crystal structure; Photochromism; Photoluminescence

1. Introduction

Photochromic compounds, which can reversibly change color or absorption spectra due to the transformation of two forms under radiation of various wavelengths [1, 2], have attracted attention because of their potential ability for optical memory, photo-optical switching, and chemical sensing [2–6]. Azo-conjugated aromatic compounds have been widely investigated due to their trans-to-cis photoisomerization reaction and the photochromism upon UV–vis or laser light irradiation [7, 8]. Photochromic properties for 3,3′-azobis-1,2,4-triazole, 1,1′-azobis-1,2,3-triazole, 5,5′-azotetrazole, and 1,1′-azobis-tetrazole and their complexes were reported [9–13]. The H_3ASA molecule, which contains azo, salicylic acid, and tetrazole moieties, should be especially desirable for photochromic compounds because it can dissociate mono-, di-, and trivalent anions, and each sort of anion can exhibit different trans/cis-enol/keto isomers based on photoisomerization reactions [14, 15]. H_2AT- and H_3ASA-based complexes, to our knowledge, are limited [9, 10, 15–17]. Here, photochromic complexes **1** and **2** are reported.

2. Experimental

2.1. *Materials and physical measurements*

All commercial reagents and solvents were used without purification unless otherwise stated. Elemental analyses were carried out using a Perkin Elmer analyzer model 240. UV–vis absorption spectra of **1** and **2** in aqueous solutions at 2×10^{-5} M L^{-1} were recorded with a U-1800 Ultraviolet–Visible Spectrophotometer. IR spectra were recorded as pressed KBr pellets on a Bruker Tensor 27 spectrophotometer. The excitation spectrum and emission spectra of **1** and **2** in aqueous solutions were recorded on an F-4500 fluorescence spectrophotometer.

2.2. *Synthesis of $[K_3(AT)_{1.5}(H_2O)_4]$ (1)*

A mixture of KI (0.033 g, 0.2 mM) and Na_2AT (0.015 g, 0.1 mM) in 10 mL of water and 10 mL of ethanol was stirred for 1 h. Yellow crystals were obtained by evaporation of the filtrate after several days, yield: 76% (based on K^+). IR (KBr, cm^{-1}): 3471s, 3065w, 2365m, 2318w, 1704w, 1643w, 1467s, 1381s, 1185w, 851s, and 576s. Elemental Anal. Calcd for $C_3H_8K_3N_{15}O_4$ (%): C, 8.27; H, 1.84; N, 48.22. Found: C, 8.29; H, 1.86; N, 48.20.

2.3. *Synthesis of $[Cd(H_2ASA)_2(H_2O)_2]$ (2)*

A solution of $CdCl_2 \cdot 2H_2O$ (0.023 g, 0.1 mM) in 2 mL of water was added to a solution of H_3ASA (0.047 g, 0.2 mM) in 10 mL of water and 10 mL of ethanol and then stirred for

5 min, and a drop of dilute HCl (2 M L^{-1}) was added to adjust the pH to about 5. The resulting mixture was filtered, and yellow crystals were obtained by slow evaporation of the filtrate after several days and washed with EtOH. Yield: 80% (based on Cd^{2+}). FT-IR (KBr, cm^{-1}): 3435s, 3129s, 1625s, 1583m, 1486s, and 1345s. Elemental Anal. Calcd for $C_{16}H_{14}CdN_{12}O_8$ (%): C, 31.23; H, 2.28; N, 27.33. Found: C, 31.26; H, 2.26; N, 27.31.

2.4. *X-ray-single crystal structure determination*

The crystals were filtered from the solution, immediately coated with hydrocarbon oil, and then put on the microscope slide. Suitable crystal was mounted on glass fiber with silicone grease and placed in a Bruker Smart APEX(II) area detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Hydrogens were added theoretically, riding on their parent atoms. Crystallographic data have been deposited in the Cambridge Crystallographic Database Center: CCDC 1002329 for **1** and 1002330 for **2**. The crystal data, details on data collection and refinement, are summarized in table 1.

3. Results and discussion

3.1. *The crystal structures*

3.1.1. The crystal structure of $[K_3(AT)_{1.5}(H_2O)_4]$ (1). Figure 1(a) shows the atomic labeling of **1**. Selected bond lengths and angles are given in table 2. Complex **1** crystallizes in the triclinic space group $P\bar{1}$. Each unit of **1** consists of three K^+ ions, one and a half trans-AT^{2-} anions, and four waters. Each K^+(1) ion coordinates to six nitrogens from four

Table 1. Crystallographic data and refinement parameters for **1** and **2**.

Complex	**1**	**2**
Formula	$C_3H_8K_3N_{15}O_4$	$C_{16}H_{14}CdN_{12}O_8$
Mr	435.54	614.80
Color	Yellow	Yellow
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.2637(3)	6.9962(10)
b (Å)	9.4455(3)	7.3291(10)
c (Å)	10.1716(3)	12.2811(17)
α (°)	87.499(2)	82.446(7)
β (°)	86.075(2)	75.431(7)
γ (°)	83.664(2)	61.970(7)
V (Å^3)	786.72(4)	537.92(13)
Z	2	1
D_{Calcd} (g cm^{-3})	1.839	1.898
F(0 0 0)	440.0	306.0
μ (mm^{-1})	0.919	1.091
Reflections collected	3621	2504
R_1^{a}	0.0292	0.0342
wR_2^{b}	0.0725	0.0962

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
$^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2]^{1/2}$.

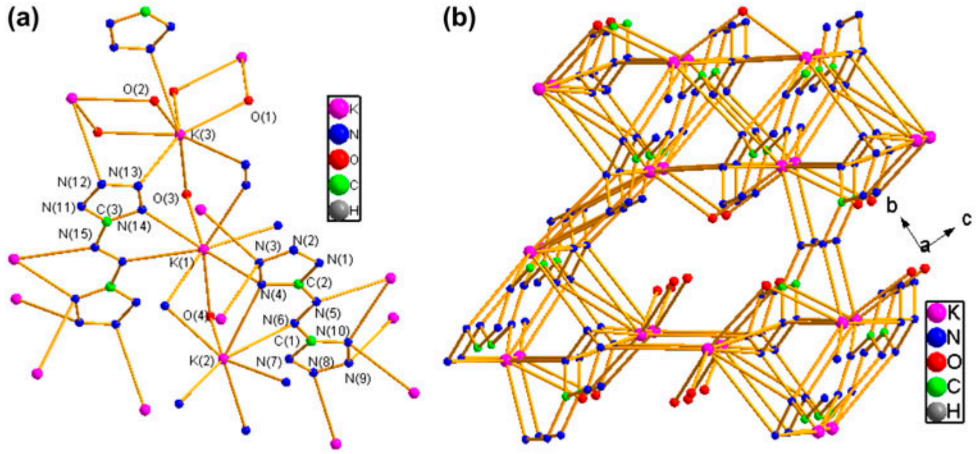

Figure 1. (a) The atomic labeling of **1**, and (b) the 3-D structure of **1**.

trans-AT^{2-} anions and two bridging water molecules to form a bicapped trigonal prism geometry [figure 1(a)]. The bond lengths of K(1)–N are 2.823–3.116 Å (table 2). The bond angles of N–K(1)–N and N–K(1)–O are 55.91(4)°–147.97(4)° and 74.24(4)°–147.97(4)°, respectively (table 2). Each K$^+$(2) ion is coordinated with six nitrogens from five trans-AT^{2-} anions and a bridging water to form a distorted monocapped trigonal prism [figure 1(a)]. The bond lengths of K(2)–N range from 2.909 to 3.084 Å. The bond angles of N–K(2)–N and N–K(2)–O are 52.78(4)°–155.92(4)° and 66.84(4)°–81.26(4)°, respectively (table 2). Each K$^+$(3) ion coordinates to three nitrogens from three trans-AT^{2-} anions and five bridging waters in a distorted bicapped trigonal prism geometry [figure 1(a)]. The bond lengths of K(3)–O and K(3)–N are ranging from 2.767 to 3.192 Å and 3.080 to 3.239 Å,

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

K(1)–N(14)	2.8228(15)	K(1)–N(3c)	3.1161(15)
K(1)–N(10a)	2.8914(15)	K(1)–O(3)	2.7144(15)
K(1)–O(4)	2.7905(15)	K(2)–N(4)	3.0839(15)
K(2)–N(9d)	2.7158(16)	K(2)–N(6)	3.0006(14)
K(2)–O(3)	2.7158(16)	K(3)–N(10a)	3.0800(15)
K(3)–N(14)	3.1859(15)	K(3)–N(12f)	3.2386(15)
K(3)–O(1)	2.7667(17)	K(3)–O(4)	2.8671(16)
K(3)–O(2)	2.8721(16)	K(3)–O(1 g)	3.1922(19)
N(15b)–K(1)–O(4)	74.24(4)	N(14)–K(1)–O(4)	77.57(5)
N(14)–K(1)–O(3)	134.43(5)	N(4)–K(1)–O(4)	147.97(4)
N(3c)–K(1)–O(4)	142.08(4)	O(3)–K(1)–O(4)	106.62(5)
N(14)–K(1)–N(15b)	55.91(4)	N(5a)–K(1)–N(15b)	143.45(4)
N(14)–K(1)–N(4)	117.94(4)	N(10a)–K(1)–N(4)	76.31(4)
N(4)–K(2)–N(6)	52.78(4)	N(6)–K(2)–O(3)	66.84(4)
N(4)–K(2)–O(3)	81.26(4)	N(9d)–K(2)–N(6)	155.92(4)
N(13c)–K(2)–O(3)	140.78(5)	N(8e)–K(2)–N(6)	88.61(4)
N(6)–K(2)–N(3c)	116.33(4)	O(1)–K(3)–O(4)	94.27(5)
O(1)–K(3)–O(2)	108.36(5)	O(4)–K(3)–O(2)	154.67(5)
O(1)–K(3)–O(1g)	68.00(6)	N(14)–K(3)–O(2)	84.01(4)
N(10a)–K(3)–O(2f)	143.81(4)	N(12f)–K(3)–O(1g)	52.40(4)
N(10a)–K(3)–N(14)	73.45(4)	N(10a)–K(3)–N(12f)	146.23(4)
N(14)–K(3)–N(12f)	134.49(4)		

Note: Symmetry codes: (a) −*x*, −*y*, 1 − *z*; (b) 1 − *x*, 1 − *y*, 1 − *z*; (c) 1 − *x*, −*y*, 1 − *z*; (d) 1 + *x*, *y*, *z*; (e) −*x*, −*y*, 2 − *z*; (f) 1 − *x*, 1 − *y*, −*z*; and (g) −*x*, 1 − *y*, 1 − *z*.

respectively. The bond angles of N–K(3)–N, N–K(3)–O, and O–K(3)–O are 73.45(4)°–146.23(4)°, 52.40(4)°–143.81(4)°, and 68.00(6)°–154.67(5)°, respectively (table 2). The trans-AT^{2-} anions are μ_7- and μ_8-bridging ligands. The water molecules are μ_2 bridges. The μ_7- and μ_8-bridging trans-AT^{2-} ligands and μ_2 waters link three kinds of K$^+$ ions to generate a 3-D structure [figure 1(b)].

3.1.2. The crystal structure of [Cd(H$_2$ASA)$_2$(H$_2$O)$_2$] (2). Figure 2(a) gives the atomic labeling diagram of **2**. Selected bond lengths and angles are shown in table 3. Complex **2** is solved in the triclinic space group *P*$\bar{1}$ with the asymmetric unit consisting of a Cd^{2+}, two

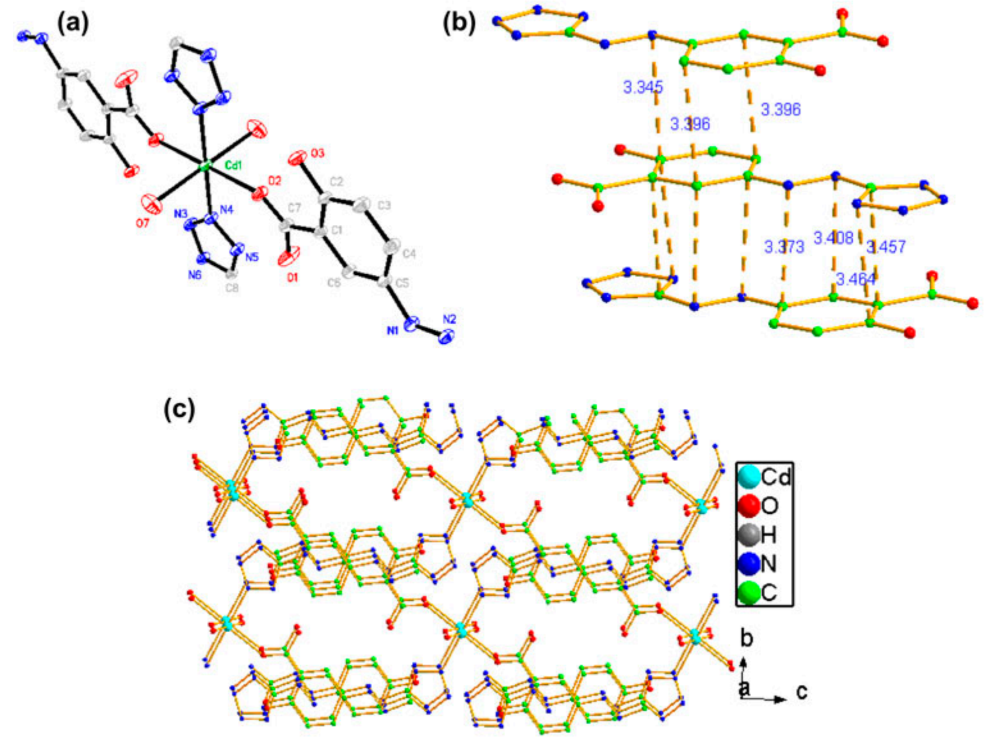

Figure 2. (a) ORTEP view (30% thermal ellipsoids) of **2**, (b) the edge-to-edge H2ASA$^-$ alignment showing the π–π stacking interaction in **2**, and (c) the 3-D supramolecular structure.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cd(1)–N(4)	2.266(2)	Cd(1)–N(4a)	2.266(2)
Cd(1)–O(2)	2.238(2)	Cd(1)–O(2a)	2.238(2)
Cd(1)–O(7)	2.240(3)	Cd(1)–O(7a)	2.240(3)
N(4)–Cd(1)–N(4a)	180.000	N(4)–Cd(1)–O(2)	97.27(8)
N(4)–Cd(1)–O(2a)	82.73(8)	N(4)–Cd(1)–O(7)	88.16(10)
N(4)–Cd(1)–O(7a)	91.84(10)	N(4a)–Cd(1)–O(2)	82.73(8)
N(4a)–Cd(1)–O(2a)	97.27(8)	N(4a)–Cd(1)–O(7)	91.84(10)
N(4a)–Cd(1)–O(7a)	88.16(10)	O(2)–Cd(1)–O(2a)	180.00(8)
O(2)–Cd(1)–O(7)	90.47(11)	O(2)–Cd(1)–O(7a)	89.53(11)
O(2a)–Cd(1)–O(7)	89.53(11)	O(2a)–Cd(1)–O(7a)	90.47(11)
O(7)–Cd(1)–O(7a)	180.00(15)		

Note: Symmetry codes: (a) $1-x$, $1-y$, $-z$.

trans-enol H_2ASA^- anions, and two waters. Cd^{2+} coordinates to two nitrogens and two O(carboxyl) atoms from four different trans-H_2ASA^- anions and two waters in an octahedral geometry. The H_2ASA^- anions show a trans-enol isomer with the bond length for C2–O3 (phenol) being 1.341(3) Å. The H_2ASA^- anions are μ_2 bridges with each anion linking two different Cd^{2+} ions resulting in a 1-D double linear chain structure. An edge-to-edge alignment between H_2ASA^- rings with the separated interplanar atom-to-atom shortest distance of 3.345 Å indicates π–π stacking interactions [figure 2(b)]. The π–π stacking interactions and electrostatic interactions link 1-D structure into a 3-D supramolecular structure [figure 2(c)].

3.2. *The photochromism*

3.2.1. The photochromism of aqueous solutions of 1. The UV–vis spectral change of **1** in aqueous solution at 2.0×10^{-5} M L^{-1} under 310 nm UV light irradiation at regular interval of time was measured. As shown in figure 3 upon 310 nm UV photoirradiation, the absorption spectrum was steadily modulated, with the extinction coefficient corresponding to π–π* electronic transition band at 310 nm wavelengths decreased, while that corresponding to n–π* electronic transition band at 420 nm wavelength increased. The molar extinction coefficient corresponding to the absorption at 310 nm decreases from $\varepsilon = 7.4 \times 10^4$ to 3.6×10^4 dm^3 M^{-1} cm^{-1}, and that corresponding to absorption band at 420 nm increases from $\varepsilon = 1.4 \times 10^3$ to 3.1×10^3 dm^3 M^{-1} cm^{-1}, suggesting that part of the trans isomer converted to the cis form in solution [2, 3]. The observation of the two isosbestic points at 270 and 375 nm in the spectra confirms the participation of the cis and trans isomers of AT^{2-} ligand, as expected [18].

3.2.2. The photochromism of aqueous solutions of 2. Figure 4 gives the UV–vis spectral changes of aqueous solution of **2** with concentration of 2.0×10^{-5} M L^{-1} and the pH of 10.1 under 365 nm UV light irradiation at room temperature. Upon irradiation of the aqueous solutions of **2** with 365 nm UV light, three absorptions at 280, and 443 nm decrease in intensity and two new absorptions at 260 and 354 nm are noted and four regions with three

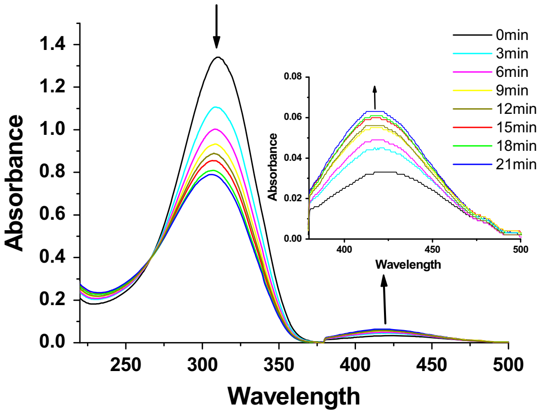

Figure 3. UV–vis spectral change of **1** in aqueous solution (2.0×10^{-5} M L^{-1}) upon repeated irradiation at 310 nm at 3-min intervals at room temperature.

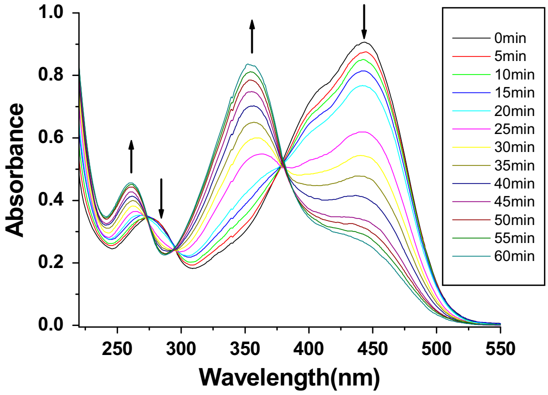

Figure 4. UV–vis spectral change of 2 in aqueous solution (2.0×10^{-5} M L^{-1}) upon repeated irradiation at 365 nm at 5-min intervals at room temperature.

isobestic points at 271, 295, and 380 nm can be distinguished. The photoisomeric reaction for aqueous solutions of **2** should originate from the trans-enol to cis-enol transitions from H_2ASA^- ligands [15].

3.3. *Photoluminescence*

3.3.1. Photoluminescence of aqueous solution of 1. Figure 5 shows the emission spectrum for aqueous solution of **1** at 2.0×10^{-4} M L^{-1} under 270 nm UV light excitation, and the insert shows the excitation spectrum with the monitored incident beam at 406 nm. The solution of **1** exhibits 406 nm emission which should be attributed to the π^*–π radiative relaxation from the excited state of AT^{2-} ligand.

3.3.2. Photoluminescence of aqueous solution of 2. Figure 6 shows the emission spectrum of aqueous solution of **2** at 1.0×10^{-4} M L^{-1} under 425 nm UV light excitation.

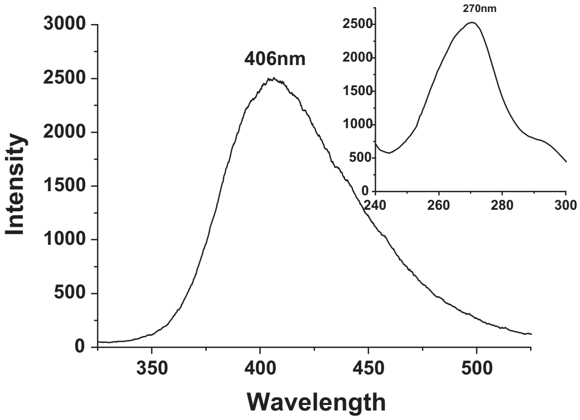

Figure 5. The emission spectrum for aqueous solution of **1**. The insert shows the excitation spectrum.

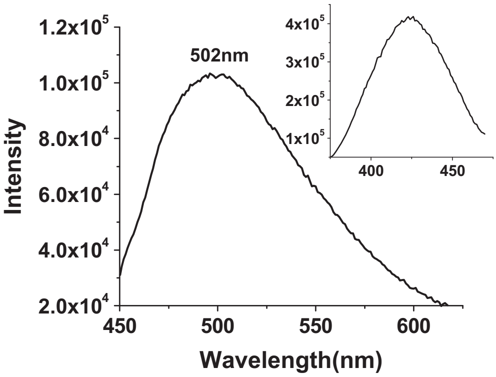

Figure 6. The emission spectrum for the aqueous solution of **2**. The insert shows the excitation spectrum.

The solution of **2** shows a 502-nm green emission band which should be attributed to the $\pi^*–\pi$ radiative relaxation from the excited state of H_2ASA^- ligand.

4. Conclusions

Two new complexes of **1** and **2** were synthesized, and their crystal structures and photochromic and photoluminescent properties were reported. This work demonstrates that both H_2AT and H_3ASA tetrazolylazo ligands can be employed to assemble varied alkali or transition metal complexes. Compared to other photochromic complexes such as $[Co(dien)_2]_2Sn_2Se_6$ reported [6], the photochromism for **1** and **2** originate from the trans–cis transition, but the photochromism for $[Co(dien)_2]_2Sn_2Se_6$ comes from the van der Waals interaction in the 3D supramolecular structure.

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